



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>C11D 11/00, 3/386</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/07989</b>  <b>(43) International Publication Date:</b> 14 April 1994 (14.04.94)
<b>(21) International Application Number:</b> PCT/EP93/02559 <b>(22) International Filing Date:</b> 20 September 1993 (20.09.93)  <b>(30) Priority data:</b> 92202964.0 25 September 1992 (25.09.92) EP <i>(34) Countries for which the regional or international application was filed:</i> NL et al.  <b>(71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB).  <b>(71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD US):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).		<b>(72) Inventors ; and</b> <b>(75) Inventors/Applicants (for US only) :</b> HAVERKAMP, Johan [NL/NL]; de Kroeskarper 40, NL-2661 KL Bergschenhoek (NL). VAN DER VLIST, Pieter [NL/NL]; Tarwestraat 5, NL-2989 AV Ridderkerk (NL). WARMOESKERKEN, Marinus, Maria, C., G. [NL/NL]; Oostsingel 204, NL-2612 HL Delft (NL). WILLEMSE, Simon [NL/NL]; Surinamesingel 31, NL-3131 XL Vlaardingen (NL).  <b>(74) Agent:</b> KAN, Jacob, H.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).  <b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CLEANING PROCESS  <b>(57) Abstract</b>  A process for cleaning articles whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy, characterized in that the enzymatic aqueous cleaning medium contains an enzyme having lipolytic activity.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

CLEANING PROCESSTECHNICAL FIELD

This invention relates to a cleaning process, and more in particular to a process for cleaning soiled articles such as fabrics, using an ultrasonic energy source. In particular, the invention relates to a process whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy.

10

BACKGROUND AND PRIOR ART

Cleaning processes whereby ultrasonic energy is used have been known in the art for many years. In such a process, the articles to be cleaned are immersed in an aqueous cleaning medium and are radiated with ultrasonic energy. In particular, numerous publications relate to ultrasonic fabric washing processes. For that purpose, the aqueous cleaning medium usually contains one or more conventional ingredients of detergent products such as surfactants, builders and the like. EP-A-258 816 (Henkel) discloses a ultrasonic fabric washing process wherein the wash load is treated with a cleaning medium having such a strong wetting capacity that the wash load is thoroughly wetted and de-aerated.

25

It is also been suggested to incorporate enzymes in products for ultrasonic fabric washing. For example, EP-A-258 816 (Henkel) suggests the use of an enzymatic aqueous medium in an ultrasonic fabric washing process. Suitable enzymes are in particular alkaline proteases. It is shown that the presence of an alkaline protease in the wash liquor has a beneficial effect on the cleaning performance of the detergent product in an ultrasonic washing process. It is mentioned but not exemplified that amylases, lipases, pectinases, nucleases and/or oxydoreductases can also be used.

35

- 2 -

Furthermore, JP-A-01026779 (Kao) discloses an ultrasonic fabric washing process whereby the cleaning solution contains a cellulase enzyme.

- 5 In his article in Chemistry and Industry 1990, pages 183-186, Malmos notes that it is known that generally the activity of lipases during a conventional washing process is low, and Lipolase (Trade mark of Novo/Nordisk) is no exception. During the drying process, when the water  
10 content of the fabric is reduced, any remaining enzyme regains its activity and the fatty stains are hydrolysed. During the following wash cycle the hydrolysed material is removed. This also explains why the effect of lipases is low after the first washing cycle, but significant in the  
15 following cycles.

- In view of these more recent findings, one skilled in the art would hardly expect any benefits from the presence of an enzyme having lipolytic activity in an ultrasonic  
20 washing process, especially when considering the short contact time which is in the order of minutes.

- Contrary to what one would expect, we have now surprisingly found that the incorporation of an enzyme having lipolytic  
25 activity into the aqueous cleaning medium of an ultrasonic washing process leads to a significant improvement of the wash performance.

#### DEFINITION OF THE INVENTION

- 30 According to the invention, there is provided a process for cleaning articles whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy, characterised in that the enzymatic aqueous cleaning medium contains an enzyme having lipolytic  
35 activity of 0.1 to 500 LU/ml. Preferably, the soiled articles are fabrics. Preferably, the cleaning medium comprises surface active agents.

- 3 -

DESCRIPTION OF THE INVENTION

In the process of the present invention, soiled articles such as fabrics are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy.

- 5 The principles of ultrasonic washing are well known in the art and can, for instance, be derived from the earlier mentioned EP-A-258 816 (Henkel). For the purpose of this application we define ultrasonic energy as usually involving frequencies of about 10 kilo Hertz (kHz) to about  
10 100 kHz, however, higher frequencies of up to 10 mega Hertz (MHz) may also be used. In general, ultrasonic energy will be applied to the enzymatic aqueous cleaning medium for about 15 minutes or less, preferably between 0.25 to 10 minutes and more preferably between 0.5 to 5 minutes.  
15 Optionally, the wash load may be agitated slowly, preferably during "pulsing periods", i.e. periods in which no ultrasonic energy is applied to the wash load.

- The enzymatic aqueous cleaning medium used in the present  
20 process comprises 0.05 to 50 g/l, preferably 0.1 to 10 g/l (most preferably up to 5 g/l) of a conventional detergent composition, which includes conventional detergent ingredients such as surface active agents, builders, etc..

- 25 The surface active agents may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by  
30 Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. The surfactants preferably comprise one or more nonionic and/or anionic surfactants. They may also comprise amphoteric or zwitterionic detergent compounds, but this is  
35 not normally desired owing to their relatively high cost.

- 4 -

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C<sub>6</sub>-C<sub>22</sub> alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C<sub>8</sub>-C<sub>18</sub> primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 10 EO. Other examples of suitable nonionic surfactants are alkyl polyglycosides and polyhydroxy fatty acid amide surfactants such as disclosed in WO-A-92/06154 (Procter & Gamble).

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C<sub>8</sub>-C<sub>18</sub> alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C<sub>9</sub>-C<sub>20</sub> benzene sulphonates, particularly sodium linear secondary alkyl C<sub>10</sub>-C<sub>15</sub> benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C<sub>12</sub>-C<sub>18</sub> alkyl sulphates owing to their favourable compatibility with lipolytic enzymes.

Surface active agents may preferably be present in amounts of from 0.1% by weight of the composition, more preferably 0.5% by weight and preferably up to 70% by weight, more preferably up to 60% by weight of the composition. For use

- 5 -

in fabric washing the level of surface active agents is preferably from 5% by weight, more preferably from 10% by weight and preferably up to 60 % by weight, more preferably up to 40 % by weight, most preferably up to 35% by weight.

- 5 For use in the mechanical washing of dishes the level of surface active agents is preferably from 0.5% by weight to amounts to about 60% by weight depending upon their type and properties. Preferably low-to non-foaming nonionic surfactant are used in properly built or highly built
- 10 compositions in amounts to 7% by weight. Higher levels of highly deterative surfactants, i.e. up to 70% by weight, preferably 60% by weight, may be used in lower builder containing active/enzyme-based compositions.
- 15 Preferably the concentration of surface active agents in the wash liquor is from 0.001 to 20 g/l, preferably from 0.05 to 10 g/l, most preferably up to 5 g/l.

- The enzymatic detergent composition used in the present
- 20 invention may further contain from 5 to 60%, preferably from 20 to 50% by weight of a detergency builder. This, detergency builder may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial
- 25 properties such as an alkaline pH, the suspension of soil removed from the fabric and the suspension of the fabric-softening clay material.

- Examples of suitable detergency builders include
- 30 precipitating builders such as the alkali metal carbonates, bicarbonates, orthophosphates, sequestering builders such as the alkali metal tripolyphosphates or nitrilotriacetates, or ion exchange builders such as the amorphous alkali metal aluminosilicates or the zeolites.

35

The characteristic feature of the process of the present invention is that an enzyme having lipolytic activity is

- 6 -

used in the ultrasonic cleaning process. In principle, any enzyme having sufficient lipolytic activity may be used in the process. Preferably a lipase derived from micro-organisms are used, more preferably a bacterial or fungal lipase. Most preferably the enzyme having lipolytic activity is selected from Thermomyces lipases or variants thereof, cutinases or variants thereof, Pseudomonas lipases or variants thereof, Fusarium lipases or variants thereof and/or Chromobacter lipases or variants thereof.

10

There are various publications on lipolytic enzymes or lipases. For example, EP-A-214 761 (Novo/Nordisk) gives detailed description of lipases derived from organisms of the species Pseudomonas cepacia, and certain uses therefor. EP-A-258 068 (Novo/Nordisk) gives detailed description of lipases derived from organisms of the genus Thermomyces (previous name Humicola) and certain uses therefor.

15

Examples of known lipase-containing detergent compositions are provided by EP-A-205 208 and EP-A-206 390 (Unilever) which relate to a class of lipases defined on the basis of their immunological relationships, and describe their use in detergent compositions and textile washing. The preferred lipases are those derived from P. fluorescens, P. gladioli and Chromobacter species.

20

25

EP-A-331 376 (Amano) describes lipases and their production by rDNA technique, and their use, including an amino acid sequence of lipase from Pseudomonas cepacia. Further lipase enzymes produced by rDNA technique are described in for example WO-A-89/09263 (Gist-Brocades) and EP-A-218 272 (Gist-Brocades).

30

In spite of the large number of publications on lipase enzymes and their modifications, only the lipase from Humicola lanuginosa has so far found wide-spread commercial

35



- 7 -

application as additive for fabric washing products. It is available from Novo/Nordisk under the trade name Lipolase®.

Other lipases that can be used in the present invention are  
5 lipases derived from Pseudomonas pseudoalcaligenes and variants thereof, e.g. Liponax®, and lipases derived from Pseudomonaas putida and variants thereof, e.g. Lumafast®.

Furthermore, it should be noted that there are a number of  
10 publications describing various hydrolase enzymes which are also capable of hydrolysing mono-, di-, or triglycerides. For example, WO-A-90/09447 (Plant Genetics Systems) discloses a cutinase enzyme from Fusarium solani pisi which is capable of hydrolysing triolein. Because there appears  
15 to be some confusion with regard to the nomenclature of these enzymes, we define an enzyme having lipolytic activity for the purposes of this patent application as any enzyme capable of hydrolysing mono-, di-, or triglycerides. The cutinase gene from Fusarium solani pisi has been cloned  
20 and sequenced (Ettinger et al., (1987) Biochemistry 26, 7883-7892). WO-A-90/09446 (Plant Genetics Systems) describes the cloning and production of this gene in E. coli.

25 The present invention also provides a number of combinations of the enzyme having lipolytic activity and further, conventional constituents used in detergent systems, to provide useful advantage in the ultrasonic removal of fatty material and material adsorbed to the  
30 fatty material in soil on textile.

The other components of such detergent compositions can be of any of many known kinds, for example as described in GB-A-1 372 034 (Unilever), US-A-3 950 277, US-A-4 011 169 and  
35 EP-A-179 533 (Procter & Gamble), EP-A-205 208 and EP-A-206 390 (Unilever), JP-A-63-078000 (Lion), and Research Disclosure 29056 of June 1988. In several useful

embodiments the detergent compositions can be formulated as described in EP-A-407 225.

- The enzyme having lipolytic activity can usefully be added  
5 to the detergent composition in the form of a granular composition, a solution or a slurry of lipolytic enzyme with carrier material (e.g. as in EP-A-258 068 and Savinase® and Lipolase® products of Novo/Nordisk).
- 10 The amount of enzyme having lipolytic activity can be chosen within wide limits. Preferably, the enzymatic aqueous cleaning medium contains 0.1 to 500 LU/ml. It is especially preferred to use about 0.5 to 50 LU/ml. In this specification lipase units are defined as they are in EP-A-  
15 258 068 (Novo/Nordisk). Similar considerations apply mutatis mutandis in the case of other enzymes, which may also be present.

- Advantage may be gained in such detergent compositions,  
20 where protease is present together with the enzyme having lipolytic activity, by selecting such protease from those having pI lower than 10. EP-A-271 154 (Unilever) describes a number of such proteases. Proteases for use together with lipolytic enzyme may include subtilisin of for example BPN'  
25 type or of some of the other types of subtilisin disclosed in the literature, some of which have already been proposed for detergents use, e.g. mutant proteases as described in for example EP-A-130 756 (Genentech), US-A-4 760 025 (Genencor), EP-A-214 435 (Henkel), WO-A-87/04661 (Amgen),  
30 WO-A-87/05050 (Genex), Thomas et al. (1986) in Nature 5, 316, and 375-376 and in J.Mol.Biol. (1987) 193, 803-813, Russel et al. (1987) in Nature 328, 496-500, and others.

- WO-A-92/08779 (Procter & Gamble) discloses liquid detergent  
35 compositions comprising a lipase and a modified bacterial serine protease, which is said to be more compatible with the lipase. The proteases are modified in that the

- 9 -

methionine adjacent to the active-site serine has been replaced by another amino acid.

The formulation of detergent compositions according to the  
5 invention can be further illustrated by reference to the Examples D1 to D14 of EP-A-407 225 (Unilever).

It should be pointed out here that the cleaning process of the present invention is not only suitable for cleaning  
10 fabrics, but the principle of the invention can also be applied in the cleaning of other soiled objects such as dishes and/or other table ware, or medical equipment.

The invention is now further and non-limitatively  
15 illustrated in the following Examples. The experimental setup is shown in Figure 1.

- 10 -

EXAMPLE 1

The following wash experiments were performed in a standard Tergotometer containing 1 l of tap water (9° German Hardness). Eight EMPA 101 (ex Eidgenössische Material-  
 5 prüfungsanstalt St. Gallen, Switzerland) test cloths of 7 x 7 cm were washed for 10 minutes at a temperature of 30°C, at an agitator speed of 100 rpm. The ultrasonic energy was supplied by a Branson ultrasonic probe having a tip of 1/8" with a mean power of 38 Watt. The operating frequency was  
 10 23 kHz. The experimental setup is shown in Figure 1. The wash liquor contained 3 g/l of a detergent product having the following composition (in % by weight):

	Dodecyl Benzene Sulphonate	11.2
15	Ethoxylated alcohol nonionic surfactant 7 EO	4.6
	Soap (pristerine 4950)	1.0
	Sodium tripolyphosphate	39.5
	Sodium carbonate	3.9
	Sodium silicate	7.3
20	Sodium carboxymethyl cellulose	0.6
	Fluorescer	0.2
	Sodium sulphate	31.7
	Water	rest

25 After the washing, the reflectance at 460 nm was used to monitor the cleaning action. The results are shown in the Table. It is clear that the lipase effect, which is the difference between the reflectance at 460 nm after the ultrasonic wash in the presence and in the absence of  
 30 lipase, increases with the lipase concentration.

- 11 -

EXAMPLE 2

Example 1 was repeated using the following detergent product at 2.6 g/l:

5	Dodecyl Benzene Sulphonate	8.0
	Ethoxylated alcohol nonionic surfactant 12 EO	1.8
	Ethoxylated alcohol nonionic surfactant 6 EO	0.7
	Ethoxylated alcohol nonionic surfactant 7 EO	2.2
	Alf5	0.8
10	Zeolite	42.0
	Acrylic/Maleic copolymer (CP5 ex BASF)	4.0
	Sodium silicate	1.0
	Calcium Dequest	0.3
	Sodium sulphate	18.0
15	Water and minors	12.6

The cleaning results are shown in the Table. It can be seen that the lipase effect for this phosphate-free formulation is significantly better than for the phosphate containing formulation used in example 1.

EXAMPLE 3

Example 1 was repeated using the following detergent product at 2 g/l:

25	Dodecyl Benzene Sulphonic acid	16.0
	C <sub>12</sub> -C <sub>15</sub> Ethoxylated alcohol nonionic surfactant 7 EO	7.0
	Monoethanol amine	2.0
	Citric acid	6.5
30	Sodium xylene sulphonate	6.0
	Sodium hydroxide	4.1
	protease	0.5
	Minors and water to 100%	

35 The cleaning results are shown in the Table. The lipase effect in this anionic-rich detergent composition is rather small.

- 12 -

EXAMPLE 4

Example 1 was repeated using the following detergent product at 3 g/l:

5	C <sub>12</sub> -C <sub>15</sub> Ethoxylated alcohol nonionic surfactant	10.5-13	EO	
				9.0
	Sodium sulphate			36.8
	Sodium carbonate			38.5
	Sodium silicate			7.0
10	Diatomeous Earth			1.9
	Sodium carboxymethyl cellulose			0.1
	Fluorescer			0.1
	Water and minors	to 100%		

- 15 The cleaning results are shown in the Table. It can be seen that the lipase effect in this nonionic-rich detergent composition is large.

Detergent Composition	Dosage (g/l)	Lipase Concentration (LU/ml)		Reflectance at 460nm after US wash		Lipase effect: Delta Reflectance	US power (Watt)
		Lipolase 30T	Lipolase 100T	+ Lipase	- Lipase		
Example 1	3.0	5.0		44.9	44.8	0.1	38.0
		15.0		43.7	42.2	1.5	17.0
		15.0		37.8	35.9	1.9	33.0
		15.0		36.8	35.3	1.5	33.0
		30.0		46.3	44.8	1.5	38.0
			15.0	48.7	44.8	3.9	38.0
Example 2	2.6		15.0	38.3	35.3	3.0	33.0
				38.8	35.0	3.8	33.0
				39.2	34.1	5.1	33.0
Example 3	2.0		15.0	29.7	29.2	0.5	33.0
Example 4	3.0		15.0	32.8	28.9	3.9	33.0

- 14 -

EXAMPLE 5

Polyester EMPA test clothes of Example 1, soiled with 3 wt% tri-glycerol-oleate, were washed with 2 liter water comprising 4.6 g Borax. The pH of the wash liquor was adjusted to 9.2 using a HCl solution, and further the liquor had 5 FH. A US bath was used at 33 kHz, 80 Watt, at 30°C for 30 minutes. The level of H<sup>3</sup> labelled glycerol in the wash liquor was determined and the detergency % (i.e. the percentage of the total soil that is removed after the wash) was determined for wash liquor without enzyme having lipolytic activity, for wash liquor comprising additionally 10 LU/ml lipolase and for wash liquor comprising additionally 10 LU/ml cutinase (derived from the cutinase gene from Fusarium solani pisi that is described in Ettinger et al., (1987) Biochemistry 26, 7883-7892). The following results were obtained.

lipolytic enzyme	detergency %
-	0
lipolase®	59
cutinase	85

The results show increased detergency for wash liquor comprising an enzyme having lipolytic activity. It is believed that the wash results will be even better when surface active agents are present, e.g. as regards anti-redeposition.



- 15 -

CLAIMS

1. A process for cleaning articles whereby soiled articles are immersed in an enzymatic aqueous cleaning medium and radiated with ultrasonic energy, characterised in that the enzymatic aqueous cleaning medium contains an enzyme having lipolytic activity of 0.1 to 500 LU/ml.
2. Process according to claim 1, wherein the cleaning medium comprises surface active agents.
3. Process according to claims 1-2, wherein the soiled articles are selected from fabrics, dishes and other table ware.
4. Process according to claims 1-3, in which the enzyme having lipolytic activity is selected from Thermomyces lipases or variants thereof, cutinases or variants thereof, Pseudomonas lipases or variants thereof, Fusarium lipases or variants thereof and/or Chromobacter lipases or variants thereof.
5. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium contains 0.5 to 50 LU/ml.
6. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium comprises 0.05 to 50 g/l, preferably 0.1 to 5 g/l of a detergent composition.
7. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium comprises from 0.001 to 20 g/l of surface active agents.

- 16 -

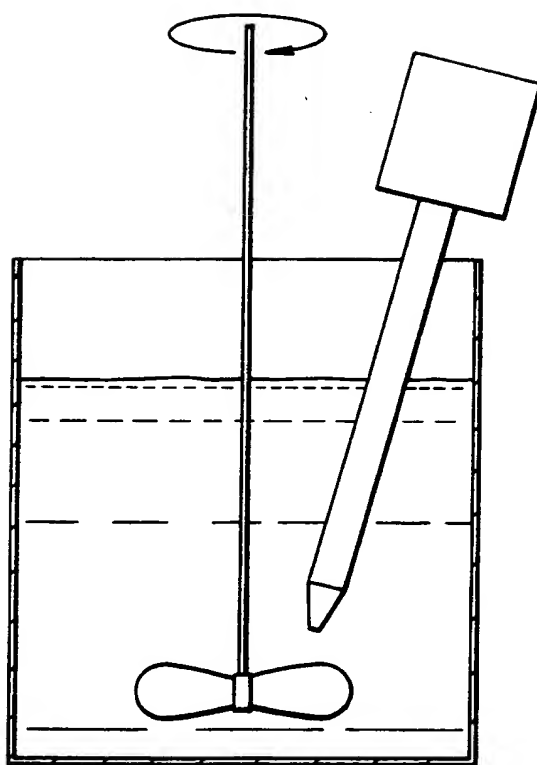
8. Process according to any one of the preceding claims, in which the enzymatic aqueous cleaning medium further comprises 0.1 to 500 GU/l of a proteolytic enzyme.

9. A process according to any one of the preceding claims, including the further step of de-aerating the aqueous cleaning medium.

10. A process according to any one of the preceding claims, wherein the ultrasonic energy is applied to the cleaning medium for 15 minutes or less.

1/1

*Fig. 1*



SUBSTITUTE SHEET

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02559

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C11D11/00 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 320 852 (NICCO BIO TECHNICA) 21 June 1989 see column 2, line 53 - column 4, line 1 ---	1,7-9
A	EP,A,0 258 816 (HENKEL) 9 March 1988 cited in the application see page 9, line 43 - page 10, line 54; example 90 ---	1,2,10
A	WO,A,88 09367 (GENENCOR) 1 December 1988 see page 6 - page 8 ---	1,2
A	EP,A,0 399 681 (CLOROX) 28 November 1990 see page 3, line 1 - line 27; table II see page 21, line 42 - line 47; table XXI ---	1,2,5
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance  
"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
"&" document member of the same patent family

Date of the actual completion of the international search

7 December 1993

Date of mailing of the international search report

22. 12. 93

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Pfannenstein, H

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 93/02559

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 407 225 (UNILEVER) 9 January 1991 cited in the application see examples d1-d14 see page 32, line 8 - line 15 ---	1,2,6-9
A	EP,A,0 258 068 (NOVO INDUSTRI) 2 March 1988 cited in the application see page 2 - page 3 ---	1,4
A	CHEMISTRY AND INDUSTRY. CHEMISTRY AND INDUSTRY REVIEW 1990 , LETCHWORTH GB pages 183 - 186 H. MALMOS 'Enzymes for Detergents' cited in the application -----	1,4

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

EP 93/02559

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0320852	21-06-89	JP-A- 1155628 US-A- 5078802	19-06-89 07-01-92
EP-A-0258816	09-03-88	DE-A- 3630183 DE-A- 3631318 DE-A- 3631727 JP-A- 63066372 ZA-A- 8706596	10-03-88 24-03-88 24-03-88 25-03-88 04-03-88
WO-A-8809367	01-12-88	EP-A- 0322429 US-A- 4981611	05-07-89 01-01-91
EP-A-0399681	28-11-90	JP-A- 3088897 US-A- 5223169	15-04-91 29-06-93
EP-A-0407225	09-01-91	WO-A- 9100910 JP-T- 4500608	24-01-91 06-02-92
EP-A-0258068	02-03-88	JP-A- 63068697 US-A- 4810414	28-03-88 07-03-89